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Y-12 G-629

# TUNGSTEN VAPOR DEPOSITION FOR REACTOR COMPONENT FABRICATION (U)
(Final Report)

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS C-66568-A-H

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UNION CARBIDE CORPORATION
Nuclear Division
Y-12 PLANT
Oak Ridge, Tennessee

July 1, 1966

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## SUMMARY

The original requirements of this order were to fabricate one 48-inch and two 21-inch vapor-deposited tungsten tubes, and vapor-deposited tungsten support tubes for both cylindrical and hexagonal fuel elements for use in the Tungsten Water-Moderated Reactor experiments. The 48-inch tube was completed and shipped; the requirement for the two 21-inch tubes was cancelled. Major emphasis was placed on developing methods for depositing support tubes integral with the fuel-element stages.

In establishing the depositing parameters, three types of mandrels were considered: (1) molybdenum, (2) Type 440C stainless steel, and (3) carbon steel. Two types of molybdenum, Y-12 pressed and sintered low density and commercial grade high density, were tested and it was determined that the commercial grade was superior. Molybdenum mandrels create little stress in the depositing, but are expensive due to their one-time use and the dissolving time required. Stainless steel mandrels have the advantage of a low initial cost and capability of reuse, but only simple shapes can be made if mandrels are to be reused, and stresses are developed in the deposits. The use of carbon steel was unsuccessful due to the difficulty in releasing the deposit from the mandrel.

A tungsten hexafluoride flow rate of approximately 120 cc/min, a hydrogen rate of 4000 cc/min (11 times the stoichiometric required hydrogen), and a depositing rate of approximately 3 mils/hr were established for these parts. Feed manifolds equipped with fan-jet nozzles were satisfactory for depositing. Similarly, manifolds with 40-mil holes deposited good parts. It was also determined that mandrel cleanliness was an absolute necessity for good depositing results.

Three methods were considered for attaching the fuel elements to the support tubes: (1) mechanical attachment with pins through a boss on the support tube; (2) by using a tungsten band integral to the fuel element and the support tube deposited onto the tungsten band; (3) by using "windows" in a sleeve mandrel to permit depositing directly to the fuel element during fabrication of the support tube.

The third method was partially unsuccessful due to the porosity in the window area which persisted even after as many as six depositing efforts. Attempts to pack molybdenum powder in these window areas to produce a suitable surface for depositing have proven unsuccessful to date. Despite the porosity in the window area, the bond strength between the tungsten support tube and the fuel-element stage was more than adequate.

# INTRODUCTION

The Oak Ridge Y-12 Plant, operated by Union Carbide Corporation-Nuclear Division for the USAEC, was authorized by the Lewis Research Center on Purchase Order C-66568-A-H to fabricate the following items for use in the Tungsten Water-Moderated Reactor experiments:

1. Vapor-deposited support tubes approximately 2.5 inches in diameter and 48 inches long with a thickness of 20 mils,

2. Cylindrical vapor-deposited tubes integral with cylindrical honeycomb fuel-element stages, and

3. Hexagonal corrugated support tubes integral with hexagonal honeycomb fuel-element stages.

Because encouraging results were realized in the initial cylindrical support-tube fabrication (Item 2), it was decided by the Lewis Technical Manager that the major effort should continue toward improving the cylindrical support tube rather than to investigate Item 3.

Tungsten was specified as the depositing material due to its: (1) high melting point, (2) good high-temperature strength, (3) high thermal conductivity, and (4) compatibility with the hydrogen propellant.

Due to limited work in this field, considerable developmental activity was required in the selection of mandrel materials and configuration, the establishment of depositing parameters, and the determination of an optimum technique for attaching the fuel element to the support tube.

# VAPOR DEPOSITING THE SUPPORT TUBES

## FACILITIES

### Deposition Furnace

The vapor-deposition facility utilized for this project is shown schematically in Figure 1. The deposition furnace or chamber consists of a cylindrical copper shell 14 inches ID by 18 inches deep with a gasketed copper lid. (A similar chamber, 72 inches deep, was used for fabricating the 48-inch tube.) A shaft through the bottom of the chamber attaches to a drive unit for both vertical and rotational movement.

The power and water leads to the induction coil enter the chamber through an insulated flange; the depositing gases are introduced through the cylinder wall. Gases are exhausted through a 1 1/2-inch copper line.

The induction coil has a nominal 4-inch ID, is 12 inches long, and is fabricated from 3/8-inch copper tubing. The turns are spaced approximately one inch from center to center. The coil for the 48-inch tube was 60 inches long with three coils in parallel electrically. All coils are water cooled.

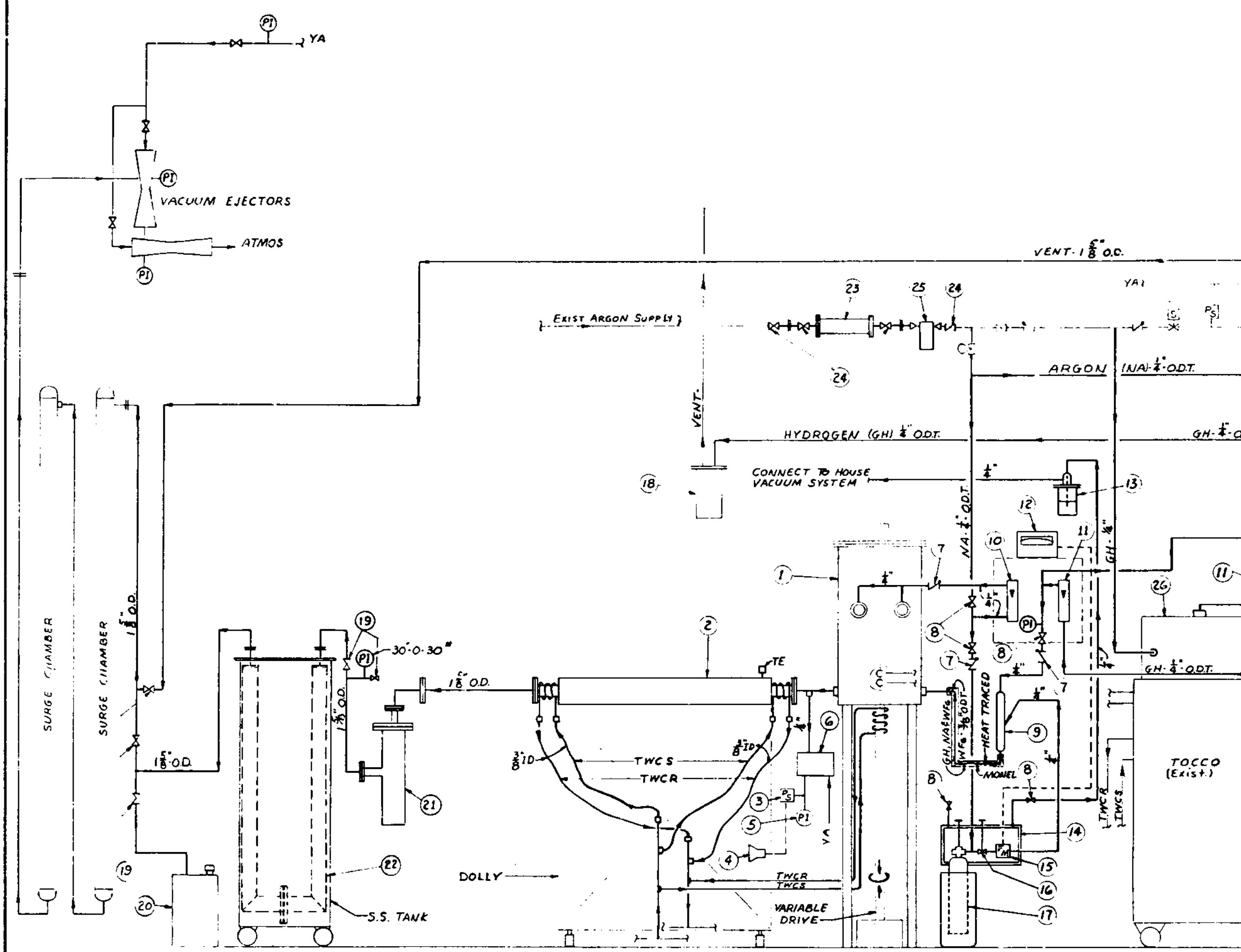
The feed manifolds are either 3/8-inch copper tubing with 40-mil holes or 3/8-inch copper tubing with spray nozzles that give a fan-jet effect. The feed is a mixture of tungsten hexafluoride and purified hydrogen gas which is passed through the manifold and directed onto the mandrel by the nozzles. The hydrogen is purified by a Milton Roy Serfass purification unit. The tungsten hexafluoride is metered through a Hastings Raydist mass flowmeter. The two feed gases pass through a mixing tube heated to 520° F prior to entering the chamber.

Power to the induction coil is supplied by a 15-kw, 10-kc water-cooled Tocco motor-generator set. Vacuum during deposition is obtained from an air-operated Jet-Vac pump.

Two views of the deposition facility are presented in Figures 2 and 3. Figure 2 shows the overall facility with its dual depositing capability with the exception of the power source; Figure 3 is a closeup view of the power source and metering equipment.

### Electric Discharge Machine

The as-received fuel elements are not dimensionally uniform. Prior to the depositing operation, these elements are made uniform by the use of a commercial electric discharge machine. An element on the bed of this machine is shown in Figure 4, a side view is shown in Figure 5, and a closeup in Figure 6. This equipment is also used for drilling specified holes in the support tube.




| MATERIAL AND EQUIPMENT TABULATION | | |
|---|---|---|
| ITEM NO. | QUAN. | DESCRIPTION |
| 1 | | VAPOR COATING CHAMBER |
| 2 | | HOT TRAP (DRAWING D-P-35757) |
| 3 | | PRESSURE SWITCH |
| 4 | | AUDIBLE ALARM |
| 5 | | PRESSURE GAUGE 0-50mm. Hg. |
| 6 | | PRESSURE INDICATOR |
| 7 | | CHECK VALVE - NUPRO |
| 8 | | NEEDLE VALVE - HOKE |
| 9 | | MIXING TUBE |
| 10 | | ROTAMETER (ARGON) |
| 11 | | ROTAMETER (HYDROGEN) |
| 12 | | INDICATOR |
| 13 | | HF TRAP (YES-4.10-6 EXCEPT MATL., 304L S.S.) |
| 14 | | VALVE AND CYLINDER ENCLOSURE (DWG. D-P-35758) |
| 15 | | FLOW METER |
| 16 | | NEEDLE VALVE - MATHESON |
| 17 | | TUNGSTEN HEXAFLUORIDE CYLINDERS |
| 18 | | SEAL POT |
| 19 | | VEECO VACUUM VALVE - SWEAT CONN'S. |
| 20 | | WELCH PUMP (EXIST.) |
| 21 | | FILTER HOUSING (DWG. D-P-35760) |
| 22 | | U-TRAP (DWG D-P-35758) |
| 23 | | MOLECULAR SIEVE |
| 24 | | VALVE GLOBE (V-6077) |
| 25 | | FILTER - CUNO MODEL 1C1AG |
| 26 | | HYDROGEN PURIFIER |

DIVISION REVIEW

NOTE:

1. All tubing Connections no[...] with a Silver Copper all[...] Classification.

| Brand Name | Manuf[...] |
|---|---|
| Silvaloy 301 | Engel[...] |
| Braze BT | Hanle[...] |
| Ambraze 72 | Americ[...] |

2. Tubing to be .030" wall Copper, [...] noted.

LEGEND:

- TWCS — Tower Water Supply.
- TWCR — " " Return.
- GH — Hydrogen.
- NA — Argon.
- YA — Instrument Air.
- $WF_6$ — Tungsten Hexafluori[...]
- TE — Temperature Element
- PI — Pressure Gauge

REF. DWGS:

- D-P-35757 — Plan And Details
- D-P-35758 — Details
- D-P-35760 — Filter Shell Detail

Figure 1. VAPOR-DEPOSITING FACILITY.

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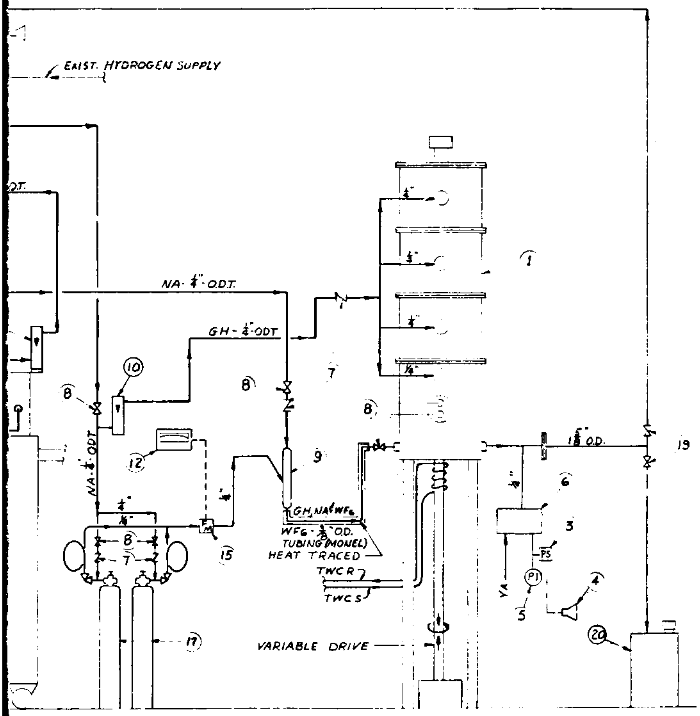
| NEXT ASSY. | FINAL ASSY. |
|---|---|
| FIN. QTY. | DESCRIPTION |

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| DEPT. | | | | |

UNION CARBIDE CORPORATION — NUCLEAR DIVISION — Y-12 PLANT

UPGRADE VAPOR COATING FAC.

VAPOR COATING FAC.

| 3 | M | P | P | SCALE: NONE | SHEET 1 OF 1 |
|---|---|---|---|---|---|
| S-2605-11 | 9998 | | E-P-57127 | | |

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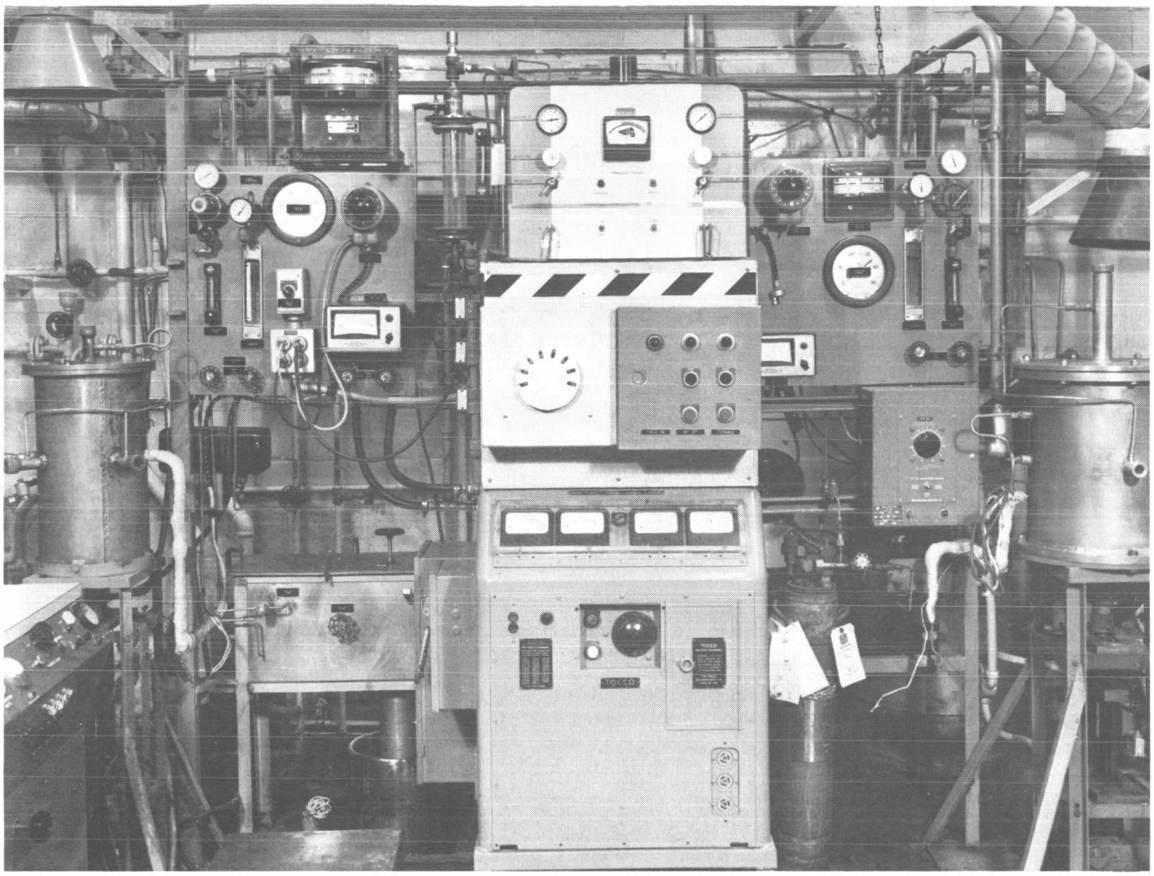

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Figure 2. DUAL DEPOSITING FACILITY.

## Grinding Equipment

The final sizing of the support tube is accomplished by use of conventional grinding machines.

## OPERATING PROCEDURE

The following operating procedure has been established for fabricating tungsten vapor-deposited parts:

1. Thoroughly clean the inside of the furnace and all equipment to be put into the furnace.

2. Mount the mandrel on the drive-shaft adapters.

3. Mount the induction coil and feed manifold. Align.

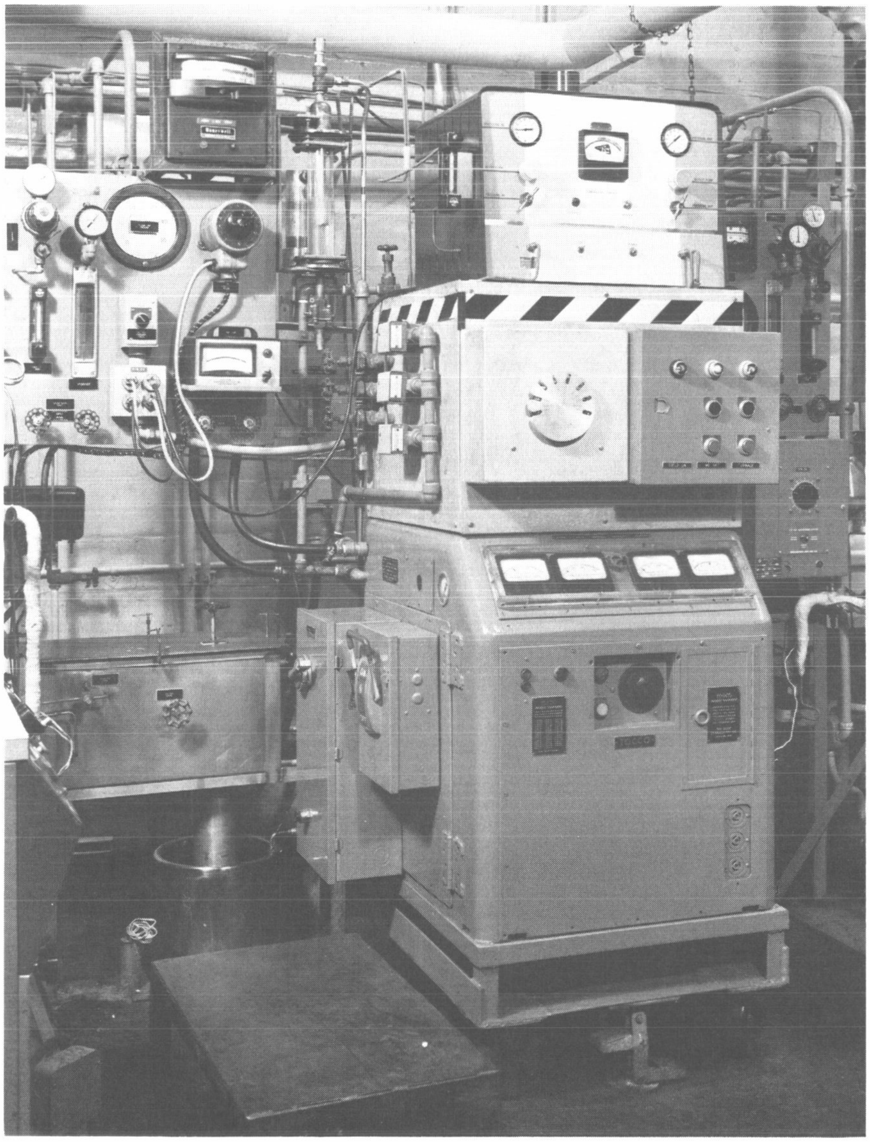

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Figure 3. POWER SOURCE AND METERING EQUIPMENT FOR THE DUAL DEPOSITING FACILITY.

4. Place the lid on the furnace and seal.

5. Pump down the system to approximately ten microns and check for leaks. The rate of rise should be less than fifteen microns/minute over a ten-minute period.

6. Start the mandrel movement.

7. Turn on the Tocco motor-generator set and power to the induction coil.

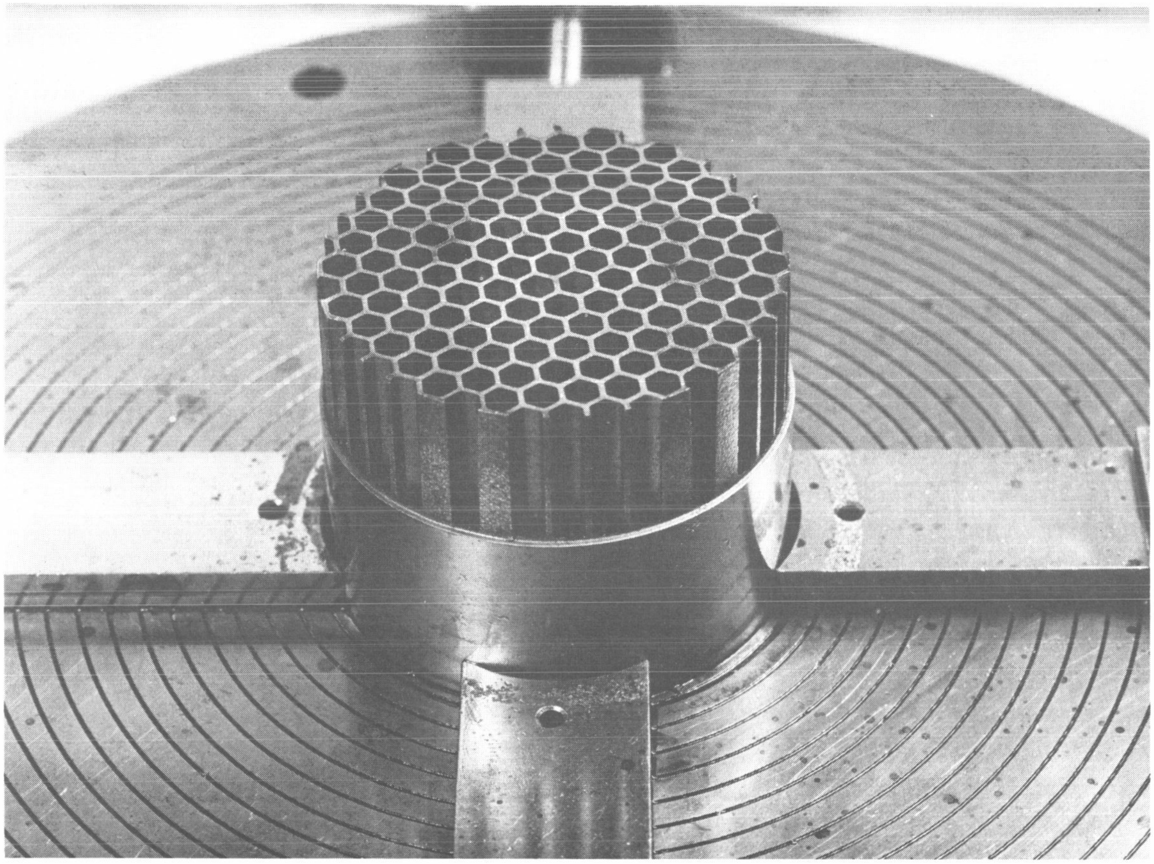

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Figure 4. FUEL ELEMENT ON THE BED OF THE ELECTRIC DISCHARGE MACHINE.

8. Heat the molybdenum mandrel to dull red (~ 600° C) under 15 - 20 mm hydrogen for one hour. If a Type 440C stainless steel mandrel is used, heat it under full vacuum for one hour.

9. After preconditioning the mandrel, turn on the tungsten hexafluoride and hydrogen gases.

10. After completion of the depositing operation, valve off the tungsten hexafluoride but leave the hydrogen and the power on for thirty minutes.

11. Shut off the power and valve off the hydrogen.

12. Backfill the furnace with argon and allow it to cool.

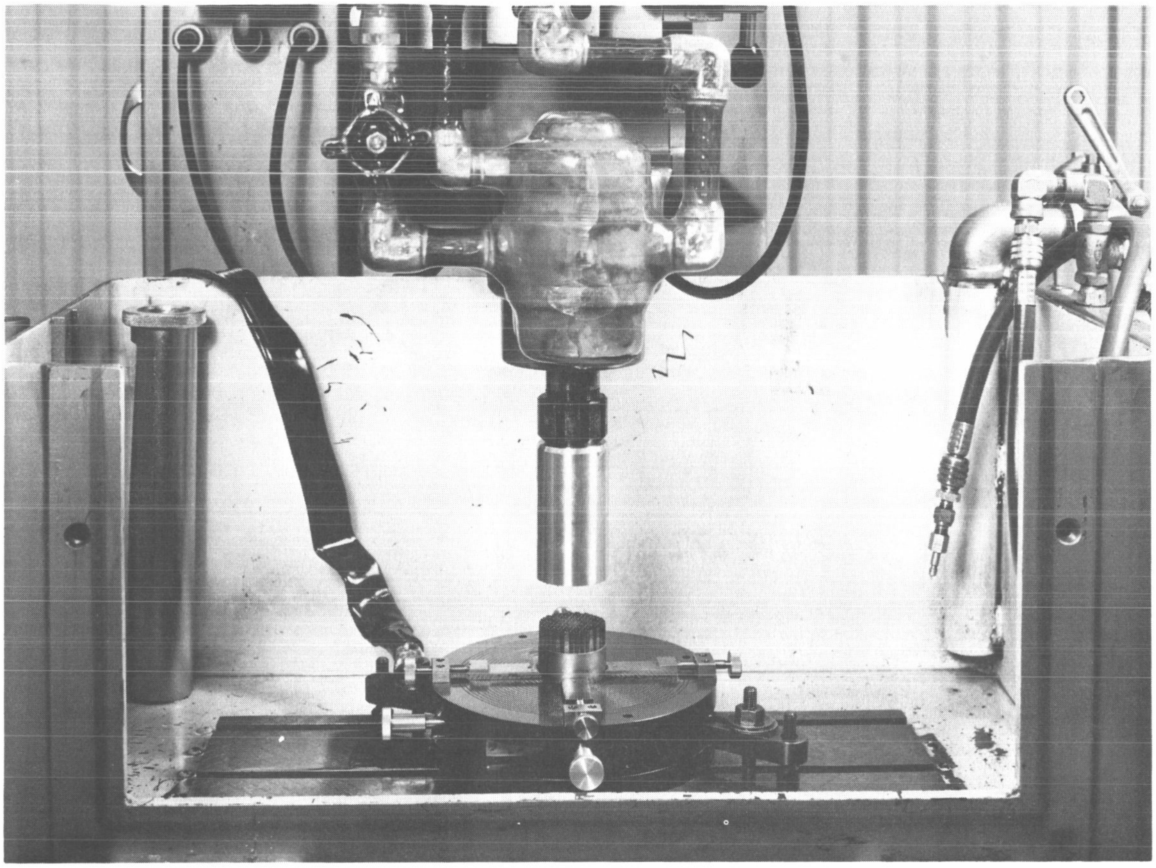

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Figure 5. ELECTRIC DISCHARGE MACHINE. (Side View)

## DISCUSSION

### Mandrel Materials

Mandrel materials for depositing tungsten by vapor deposition (chemical vapor deposition) must possess compatibility with tungsten hexafluoride, hydrogen, and hydrogen fluoride gases at elevated temperatures, and the ability to be separated from the deposited tungsten leaving the tungsten intact. These materials fall into two groups: (1) those having a coefficient of thermal expansion similar to tungsten (ie, molybdenum and graphite), and (2) those having a much higher coefficient of expansion than tungsten (ie, steel and stainless steel).

Group I - In the case of those materials having a coefficient of expansion similar to tungsten, the tungsten and the mandrel cool to room temperature from the depositing temperature still bonded together. Removal of the mandrel from the tungsten by chemical dissolution or by mechanical means is required to produce a free-standing tungsten part.

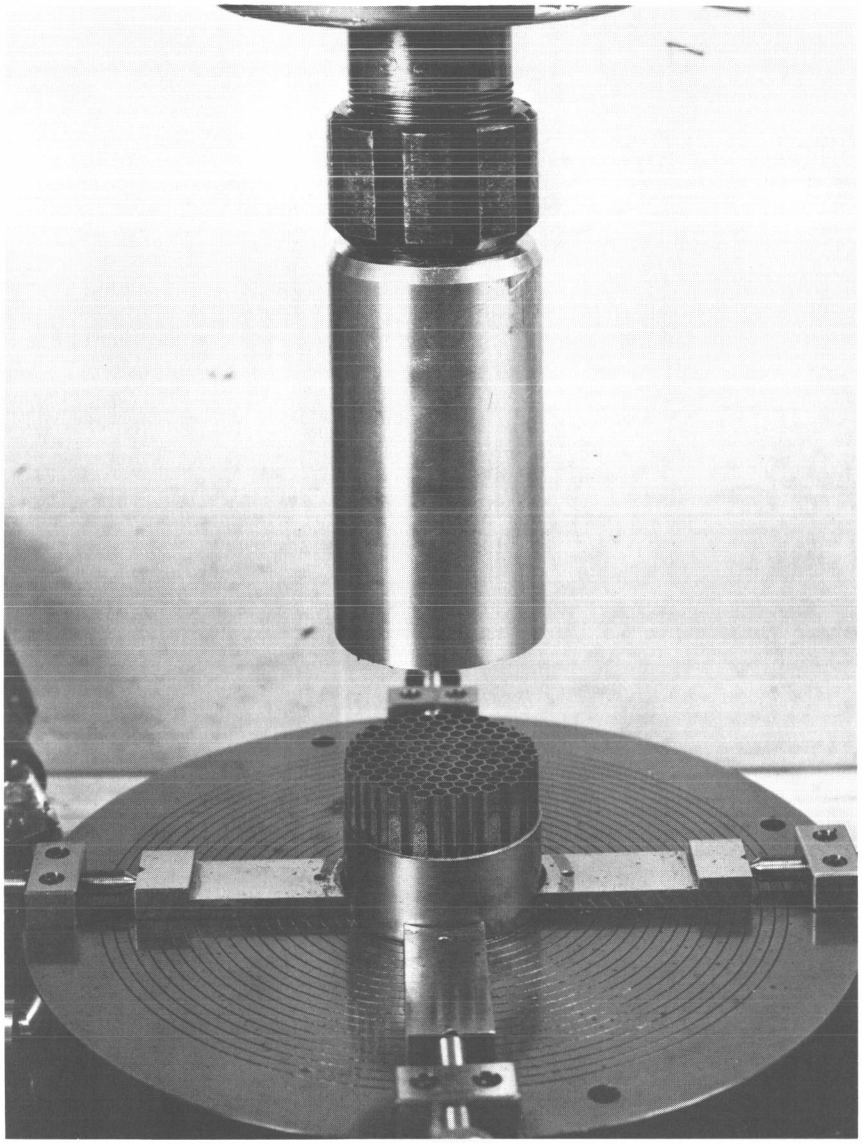

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Figure 6. ELECTRIC DISCHARGE MACHINE. (Closeup of Figure 5)

Group II - In the case of mandrels with a coefficient of thermal expansion exceeding that of tungsten, the differential shrinkage between the tungsten and the mandrel upon cooling from the depositing temperature will generate a stress which will cleave the bond between the tungsten and the mandrel. The tungsten part is merely lifted from the mandrel. If the surface character of this type of mandrel is not changed significantly, it can be hand cleaned and reused.

In general, molybdenum mandrels have proved to be the most satisfactory for general usage. The slight difference in the coefficients of thermal expansion leaves little stress in the tungsten parts deposited on molybdenum. If additional processing is necessary (such as grinding or other machining operations), the molybdenum mandrel gives excellent reinforcement. With moderate precaution, tungsten parts produced on molybdenum mandrels can be handled with little fear of breakage. Complex shapes can be produced, limited only by the ability to preshape the molybdenum and the absence of sharp reentry angles. Two types of molybdenum mandrels have been used: (1) high-density molybdenum formed by powder metallurgy and available from commercial vendors, and (2) low-density molybdenum pressed isostatically at 22,500 psi and sintered at 1000° C for five hours under vacuum. The latter material has good machinability but is porous and has little strength. The molybdenum mandrels have a surface finish of 32 microinches or better. Molybdenum has certain disadvantages, namely: it is an expensive material, becomes expendable as a mandrel, and requires a time-consuming operation to dissolve the material. However, the metal can be dissolved very inexpensively.

Success has been experienced in the use of stainless steel of the "400" series as a reusable mandrel material. Members of the "300" series have been used successfully, but surface changes after about two deposition runs cause the tungsten to stick tightly to the mandrel. In this program, a Type 440C stainless steel mandrel with a surface finish of 4 to 6 microinches has been reused as many as four times. The mandrel is cleaned after each run with 400-grit abrasive paper. The advantage of this type of mandrel is that it has an inexpensive material cost, is reusable, and is available for other parts immediately after depositing. Disadvantages are that high stresses develop in the deposit and only simple shapes such as cylinders and cones can be considered for mandrel reuse. The stresses limit depositing to thick-wall parts only (> 40 mils) and may require support for subsequent processing operations.

An innovation used during the early reuseable-mandrel studies was to heat the mandrel and part very gently to approximately 50° C above the deposition temperature immediately after the hexafluoride was shut off. This post-deposition heatup stresses the bond between the tungsten and mandrel and produces a stress in the tungsten in tension. The heatup also provides an extra 50 degrees of temperature above the ductile-brittle transition point to allow differential shrinkage to take place and thus permit the tungsten and mandrel to separate at a higher temperature. This procedure produced several parts which were dimensionally stable and withstood normal handling for several months, but it has not been applied to NASA part production.

## Deposition Parameters

Tungsten vapor deposition is the result of the reaction between tungsten hexafluoride and hydrogen according to the following reaction:

$$WF_6 + 3\,H_2 \longrightarrow W + 6\,HF.$$

[redacted]



The reaction temperature is between 300 and 1000° C. The gaseous mixture, if adsorbed on a hot surface, reacts to deposit tungsten on the surface and liberate hydrogen fluoride. This reaction will take place under widely varying conditions of temperature, pressure, and gas concentration, all of which can have a marked effect on the character of the tungsten deposit. At Y-12, absolute pressures from 6 to 20 mm (Hg), temperatures in the range of just visible under nearly black-body conditions (~600° C), and a hydrogen gas concentration of 5 to 15 times the stoichiometric requirements, yield a tungsten deposit which is pure and fine grained.

The process parameters and equipment design must be established for each part geometry, and the induction coil, feed manifold, and flow rates must be mated to a particular part in order to achieve depositing uniformity. It is believed that with a nominal number of pilot runs, the as-deposited thickness can be held within ± 10% of the nominal deposition thickness.

The deposition rate is dependent on many variables: vapor flows, vapor ratios ($WF_6/H_2$), mandrel temperatures, deposition chamber pressures, and feed manifold design. Depositing rates are increased by increasing the gas flow rates, $H_2/WF_6$ ratio, and mandrel temperature. Higher depositing rates generally result in coarser surfaces with heavy deposits on such areas as points and sharp edges, and more pronounced nodular growths. A successful deposition rate of 3 to 4 mils per hour was achieved in this program.

## Cleanliness

Cleanliness in vapor deposition cannot be overemphasized. Any foreign substance introduced into the system is a potential initiator of nodular growth. Lint from rags, tissues, and other cleaning materials needs to be given particular attention.

The deposition chamber and components need to be thoroughly cleaned before each use and should be protected while in standby status. The feed and purge gases and supply lines can also be a source of impurities.

If silicone vacuum grease is exposed to the waste gases it will react with the hydrogen fluoride, creating a volatile compound which is one basis for poor deposits. During some of the fuel-element redepositing runs it is probable that some residue from the grinding operation left a film deposit on the surface to be redeposited. When deposited, a poor bond between the tungsten layers was noted. Results of inadequate cleaning can be seen in Figure 7.

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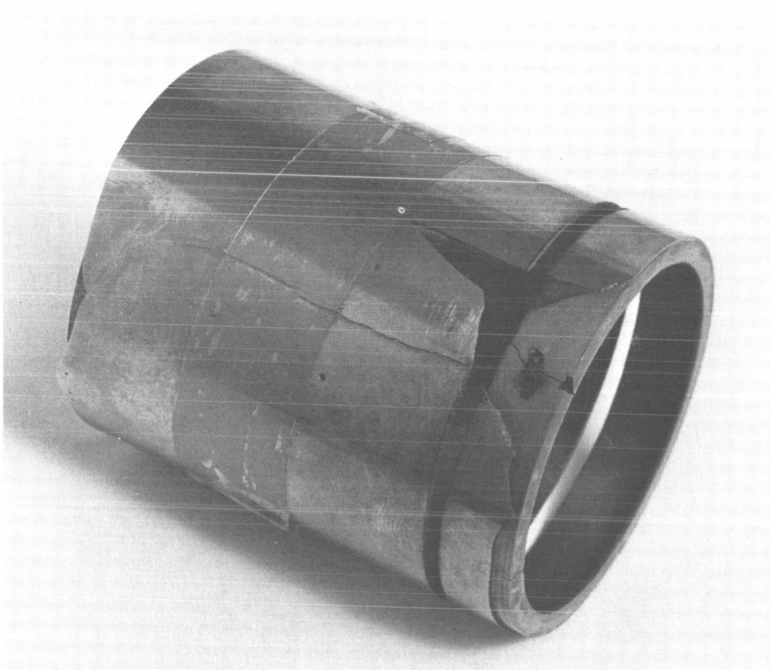

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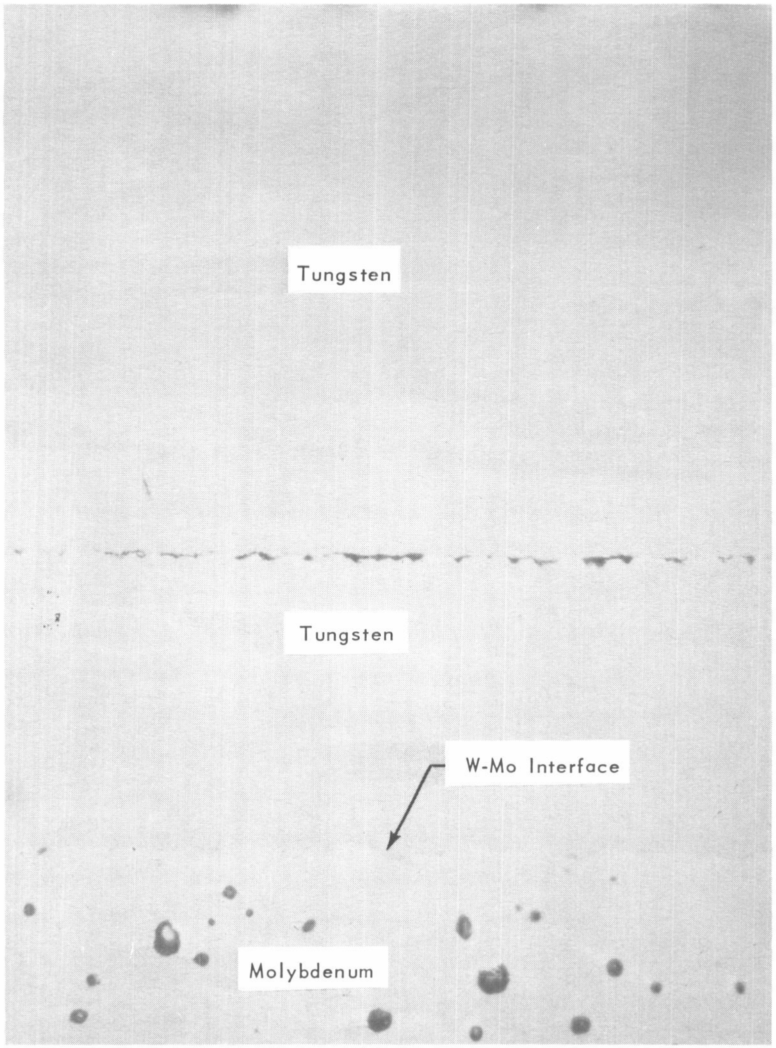
Figure 7. RUN WITH POOR BOND BETWEEN LAYERS.

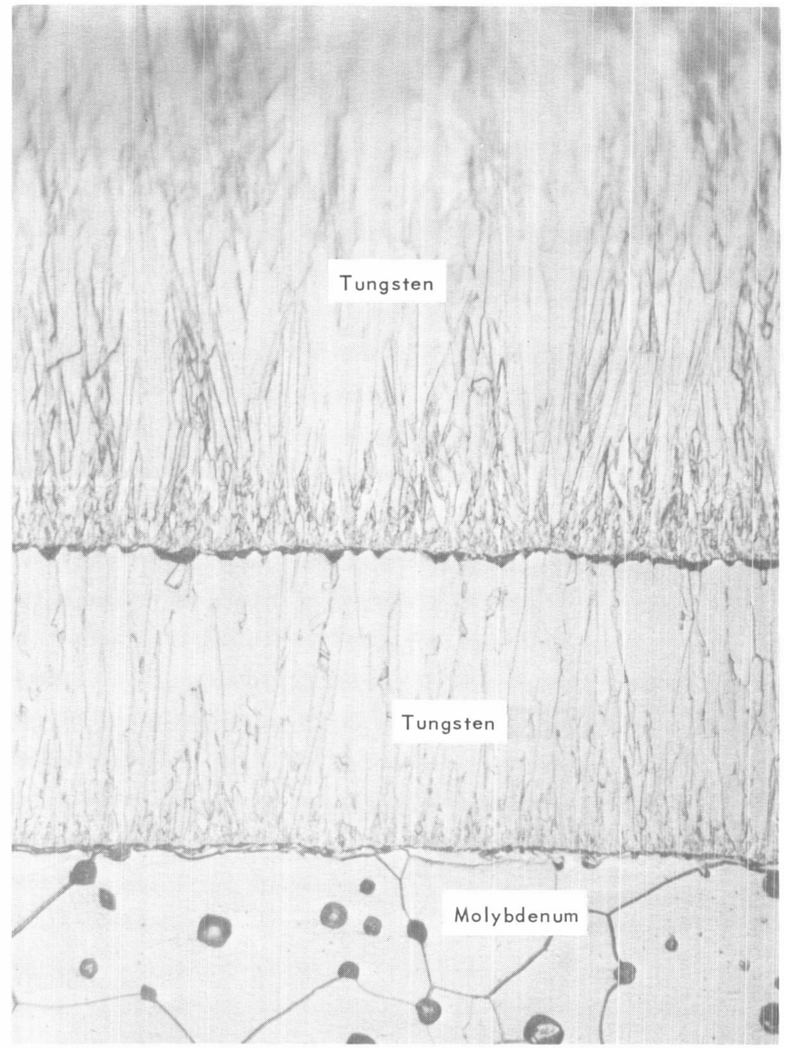
Figure 8 is an example of tungsten deposited on molybdenum and tungsten redeposited on tungsten. View (a), the as-polished structure, shows that the molybdenum-tungsten interface has little discontinuity, but the tungsten-tungsten interface is a sharp discontinuity. View (b) is a similar area which has been etched and shows an even greater discontinuity at the tungsten-tungsten interface. Since both interfaces were given essentially the same cleaning preparation before depositing, it would appear that tungsten is more difficult to clean than molybdenum and that special preparation is necessary before redepositing tungsten on vapor-deposited tungsten.

## Stresses in the Vapor-Deposited Tungsten Parts

As mentioned previously (Page 10), a primary source of residual stress in vapor-deposited tungsten parts is the differential thermal expansion between the tungsten and substrate material. In the case of the reuseable mandrels, which depend on differential thermal expansion to generate the stress necessary to separate the tungsten parts from the mandrel, the residual stresses are quite high. This condition is amply illustrated by the action of the tungsten part which was deposited on a stainless steel mandrel and somehow managed to cool to near room temperature without separating from the mandrel. When the part was placed on a table in the work area, the tungsten literally exploded from the mandrel, thoroughly fragmented, and caused the mandrel which weighed several pounds to jump off the table.




(a) As Polished C 434-4(a)




(b) Etched with $K_3Fe(CN)_6 + NaOH$ C 434-4(b)

Figure 8. TUNGSTEN VAPOR DEPOSITED ON MOLYBDENUM AND THEN REDEPOSITED ON THE VAPOR-DEPOSITED TUNGSTEN. (Bright Field Illumination; 500X)



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Another source of residual stress is the variation in temperature during deposition. If the tungsten is deposited out at varying temperatures, the layers of tungsten will constrict and thus stress each other as the deposition temperature changes throughout the run. However, the magnitude of these stresses is slight because they are generated at elevated temperatures.

In the case of reuseable mandrels, residual stresses cannot be avoided but can be minimized by causing the tungsten and mandrel to separate at as high a temperature as possible. It is vital that the separation take place above the brittle-ductile transition temperature of the vapor-deposited tungsten. Above this temperature ($\sim 200^{\circ}$ C), the tungsten part can relieve the more severe stresses through deformation; below this temperature the tungsten cannot deform except by fracturing. But, the stresses generated must exceed the bond strength between the mandrel and tungsten part for them to separate and thus some residual stress must exist in the as-deposited part.

Fluorine and fluoride impurities have been suggested as the possible source of excessive stresses and porosity in the vapor-deposited tungsten. Two recent deposition failures were analyzed for fluorine content and found to have less than 1 ppm, but this low value does not eliminate these impurities as a problem. Sampling for fluoride concentration will be continued as material becomes available.

Heat-treatment studies on vapor-deposited tungsten have indicated that a one-hour heat treatment at $1000^{\circ}$ C or higher is adequate to produce a thorough stress relief.

## Machining Vapor-Deposited Tungsten

Machining vapor-deposited tungsten is difficult because the material is hard and brittle. The material's hardness requires grinding rather than conventional lathe-turning operations; the material's brittleness requires rigid support of the workpiece or flexure and vibration will cause fracture of the workpiece.

Grinding experiments have been performed on vapor-deposited tungsten using two surface speeds—$\sim 3000$ and $\sim 5500$ ft/min. Silicon carbide proved to be the best wheel material at 5500 ft/min and aluminum oxide was best at 3000 ft/min. The best overall results were obtained with the aluminum oxide wheels and this material is recommended for conventional machining of vapor-deposited tungsten though metal-removal rates are slow and wheel wear is considerable.

An attempt was made to electrochemically grind vapor-deposited tungsten during which a modified Hammond electrolytic tool grinder was used with a Copperdyne electrolytic grinding wheel and a commercial electrolyte. Again, a low metal removal rate was experienced, probably because the modified grinder was not sufficiently rigid.

[redacted]

Fuel Element-to-Support Tube Attachment

Three methods for attaching the fuel element to the support tube have been considered: (1) band attachment, (2) mechanical pin attachment, and (3) window attachment. Each of these methods is described in the sections that follow.

Band Attachment - In this technique, a pure tungsten band integral to the fuel element is exposed to the depositing gases, and the fuel element is welded to the support tube as the tube is formed. All but 1/8 to 1/4 inch of the band is removed by electric discharge machining. A typical operation is shown in Figure 6. In Group I the band is centered on the element while a thin-walled molybdenum tube masks the balance of the fuel element and acts as a mandrel to receive the deposit for the support tube. Illustrations of the unit prior to deposition are presented in Figures 9 and 10, and after deposition in Figure 11.

No special problem was encountered in the depositing operation; however, cracking occurred during the grinding operation at the interface of the deposited tube and tungsten band. In Group II the band was located at the edge of the element, as shown in Figure 12. In this experiment both high and low-density molybdenum were used as mandrel material with the appearance indicated in Figure 13. After depositing and grinding, a crack occurred in the support tube similar to Group I, as depicted in Figure 14.

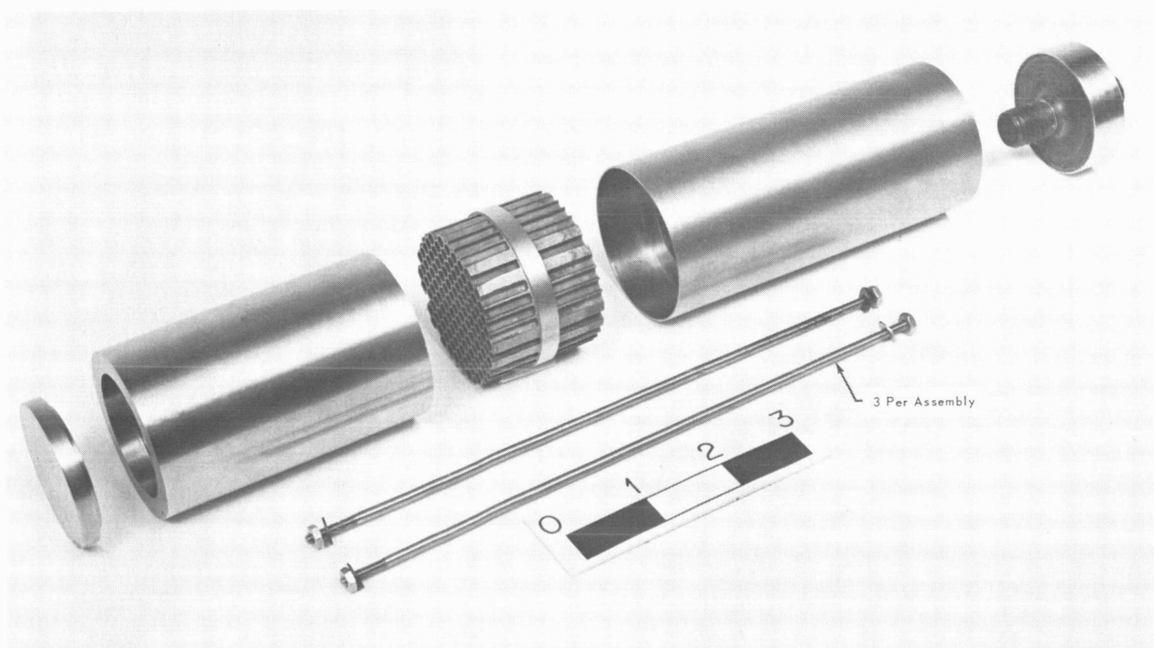


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Figure 9. BAND ATTACHMENT COMPONENTS. (Band Centered on the Element)

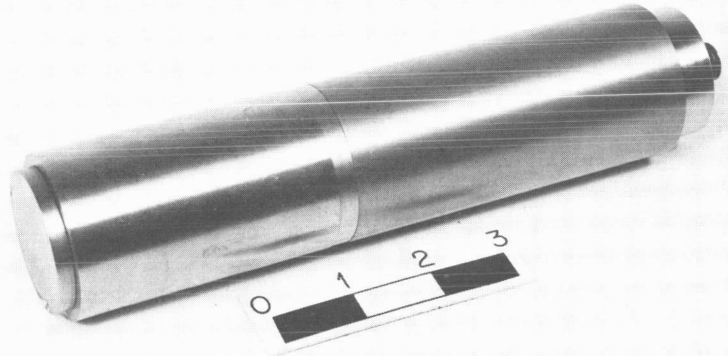


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Figure 10. BAND ATTACHMENT ASSEMBLY PRIOR TO DEPOSITION.

Mechanical Attachment - In this technique, the attachment of the fuel element to the support tube is by the use of pins. The support tubes were fabricated with a boss, as shown in Figures 15 and 16. These tubes were forwarded to the Lewis Research Center for further evaluation of this method.

Window Attachment - In this technique, the fuel element is bonded to the support tube through "windows" cut in the mandrel sleeve. A mandrel machined for a two-element assembly is seen in Figure 17. Figures 18 through 20 are additional views of this two-element assembly. Note that the fuel-element surface at the window area is uneven (Figure 17). In order to match up the fuel elements and/or align them with the mandrel, machining of the elements is required. This step results in the exposure of uneven cells (0.100" W x 0.100" D) as deposition surfaces. Rapid build-up at the cell webs results in bridging over the deposit, and subsequent grinding to the desired wall thickness exposes the open cell. In order to produce a more even surface at the window area, attempts were made to press molybdenum powder around the fuel element as shown in Figure 21, followed by sintering and machining. However, the pressure necessary to bond the powder damaged the fuel element. Another attempt was made to fill the open cells with soft molybdenum powder and soft copper foil, but without success because the powder sifted out due to gravity and vibrations. The soft copper was helpful but, because of the inability to obtain a smooth continuous substrate, rapid buildup occurred at points and left small holes in the deposit, as can be seen in Figure 22. These holes were very difficult to fill due to the extremely slow buildup on the inside wall of the hole to obtain the desired wall thickness of the support tube. Even after six redeposition attempts, the holes persisted.

## VAPOR DEPOSITION RUNS

A summary of the tungsten vapor-deposition runs performed to date is presented in Table 1. A review of this work follows.

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Figure 11. BAND ATTACHMENT AFTER DEPOSITION. (Center Band)

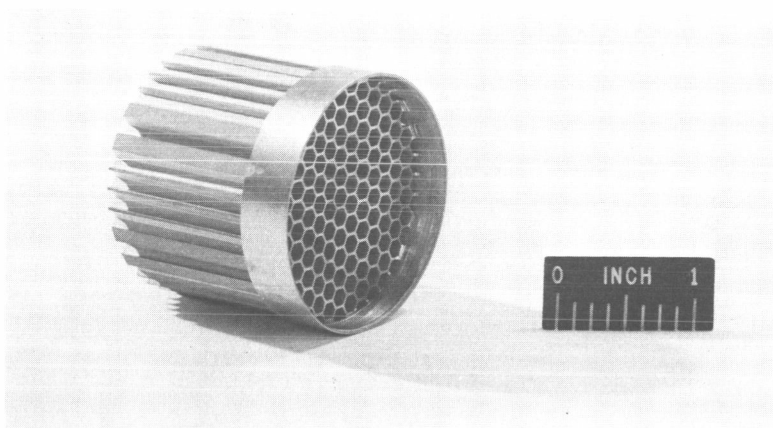


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Figure 12. BAND ATTACHMENT AT THE END LOCATION.

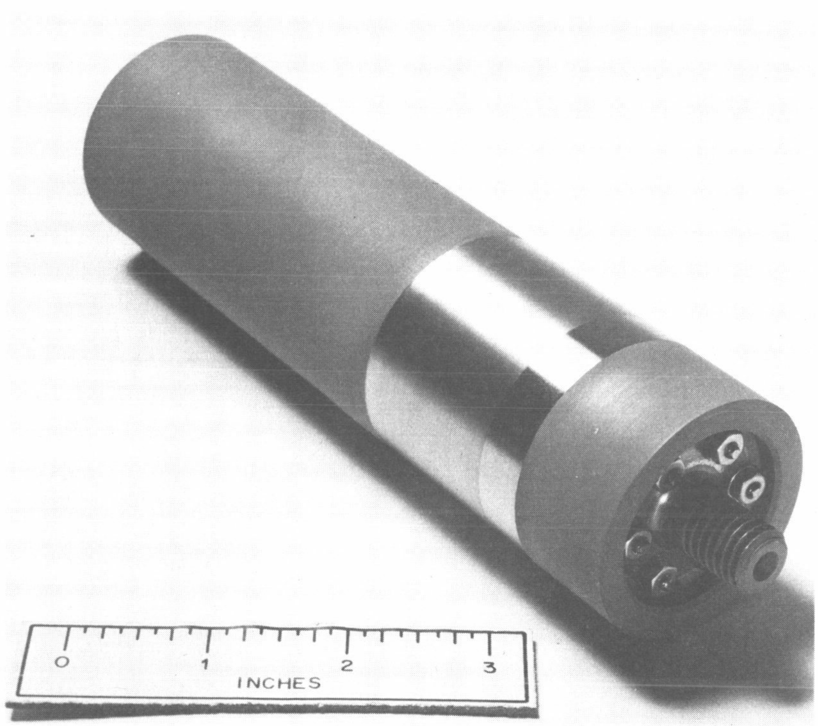


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Figure 13. BAND ATTACHMENT ASSEMBLY PRIOR TO DEPOSITION. (Band Located at the End of the Element)

## Mandrel Development

Six runs on mandrels other than molybdenum have been made in conjunction with mandrel development and establishing depositing parameters. Four of these runs were conducted on mandrels made of Type 440C stainless steel, one on copper-plated


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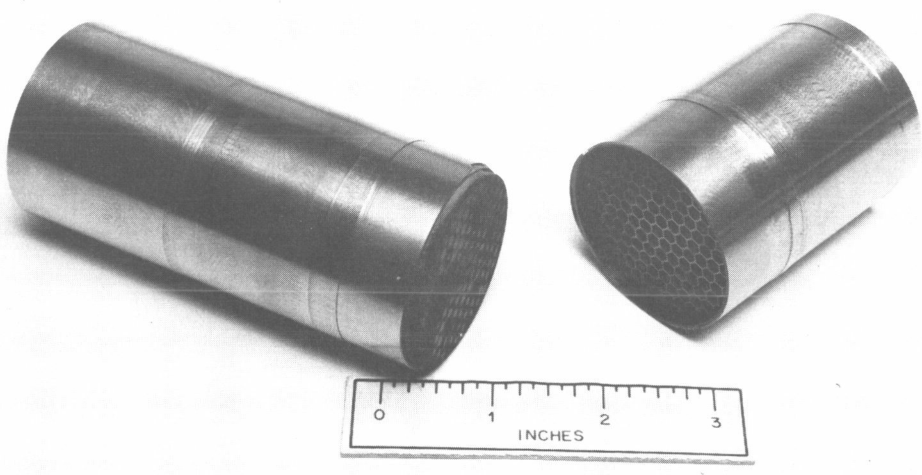
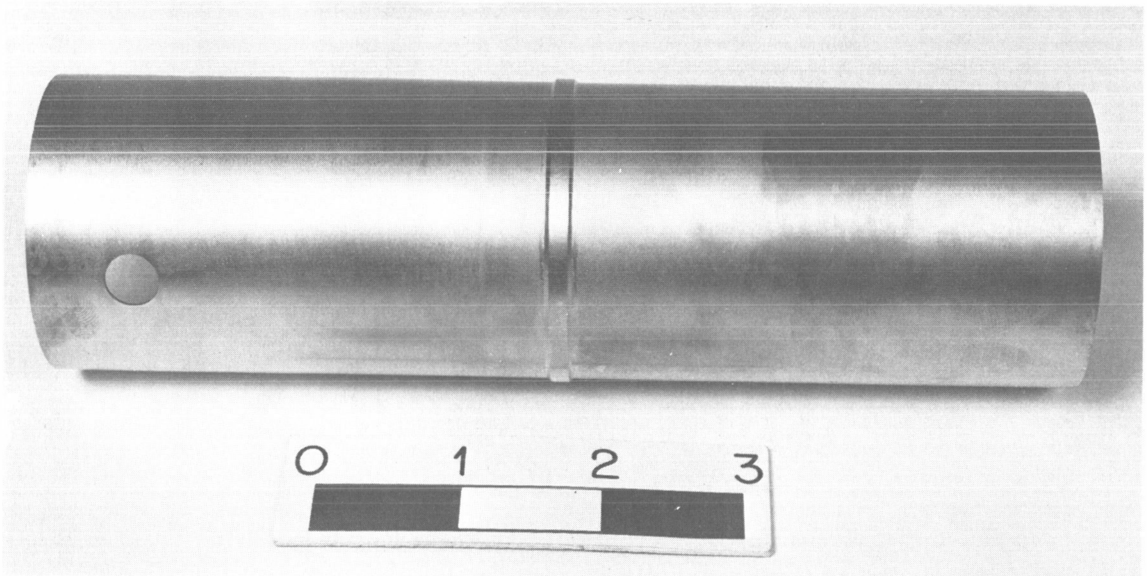


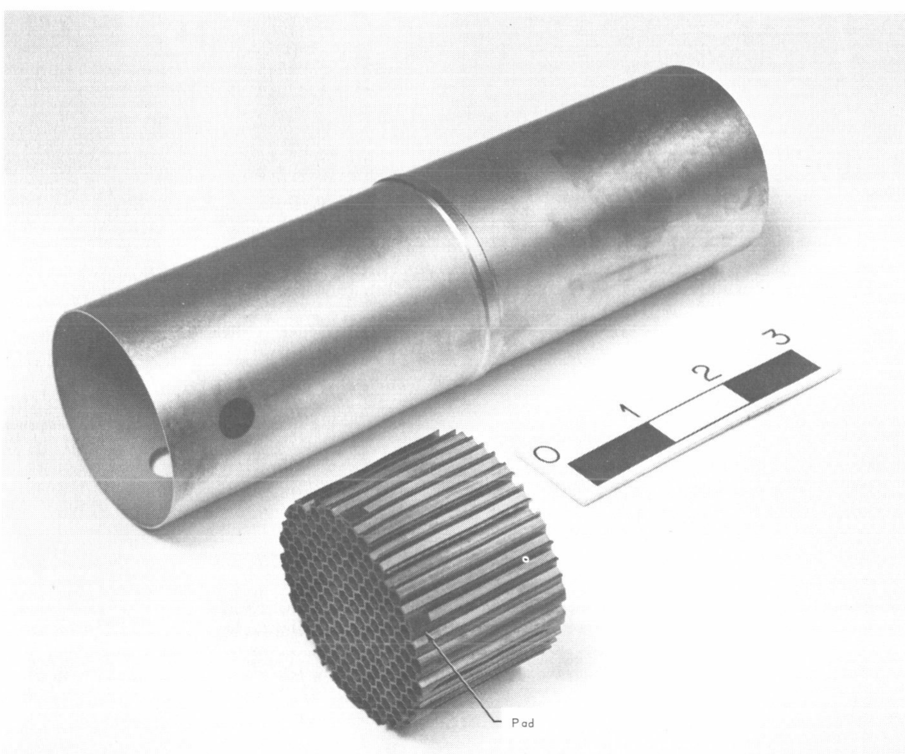

116886(C)

Figure 14. BAND ATTACHMENT AFTER DEPOSITION. (End Band)



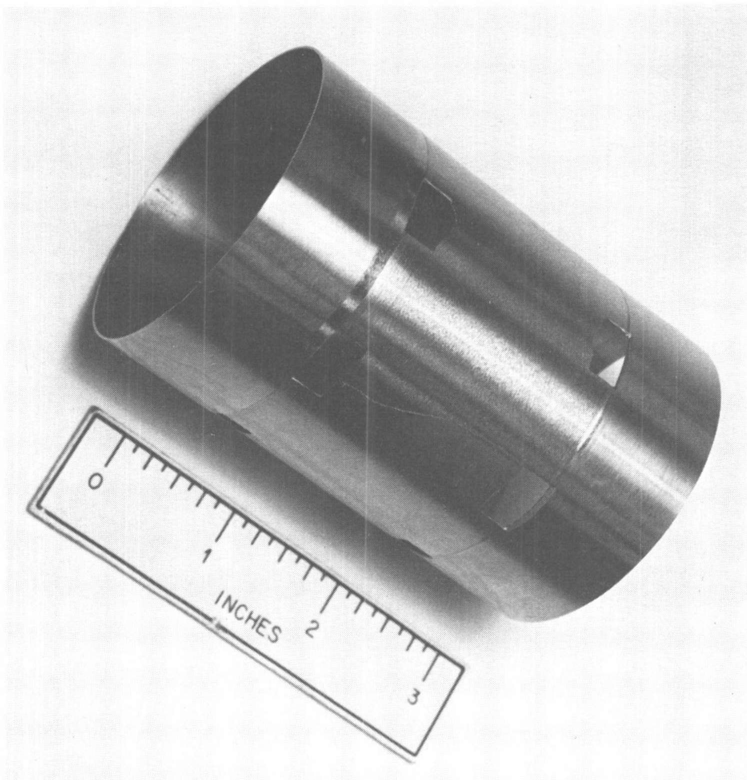

119125(U)

Figure 15. MECHANICAL ATTACHMENT SUPPORT TUBE.



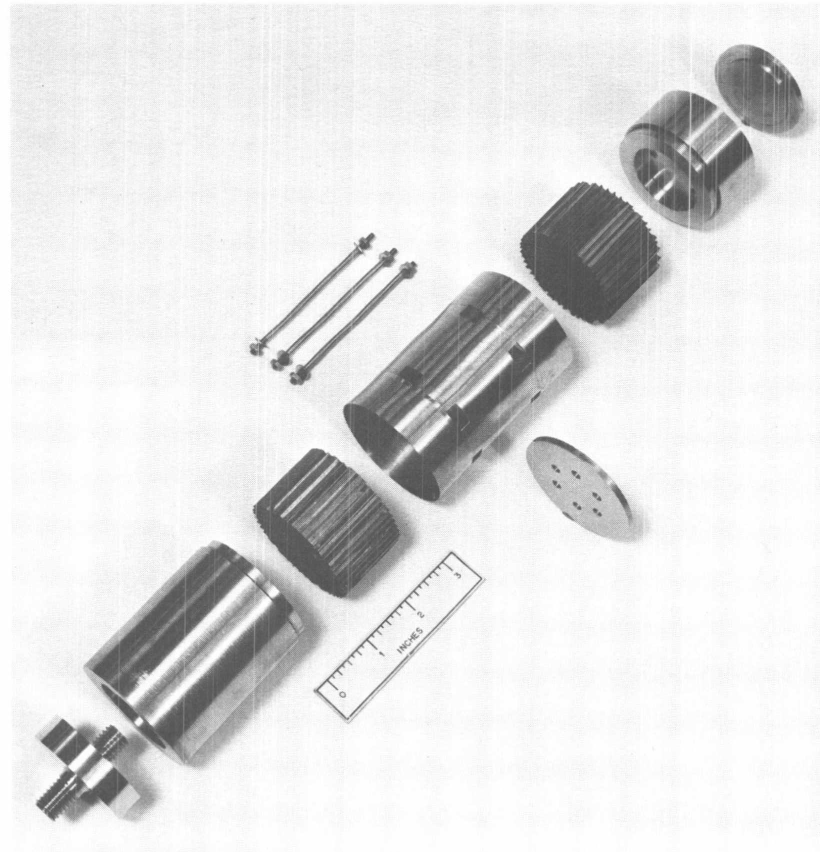

119124(C)

Figure 16. MECHANICAL ATTACHMENT COMPONENTS.



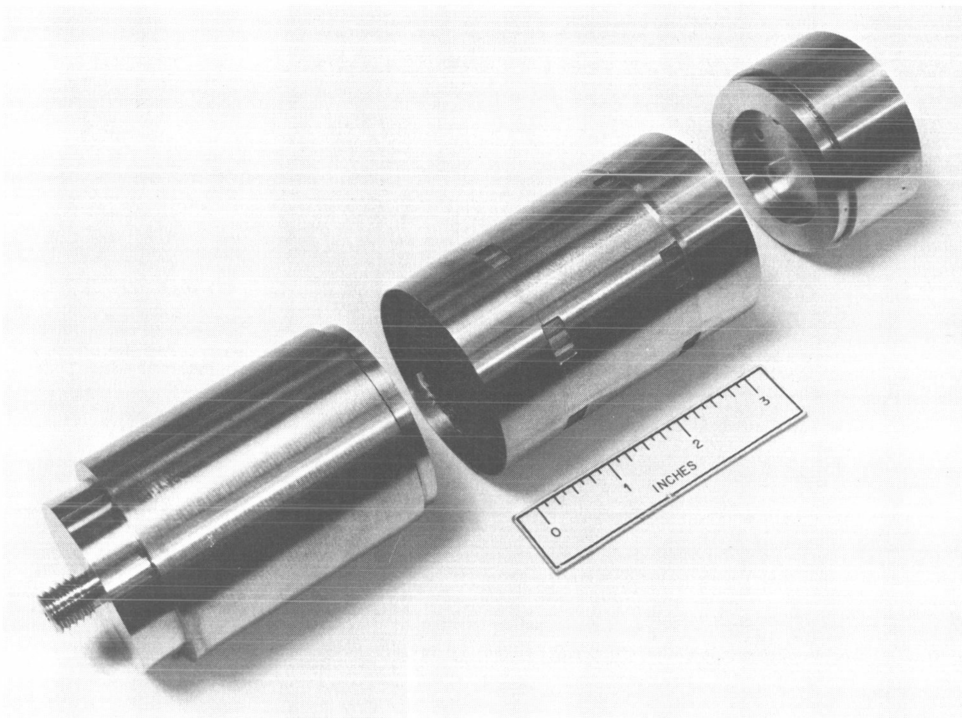

117599(U)

Figure 17. WINDOW ATTACHMENT MANDREL.



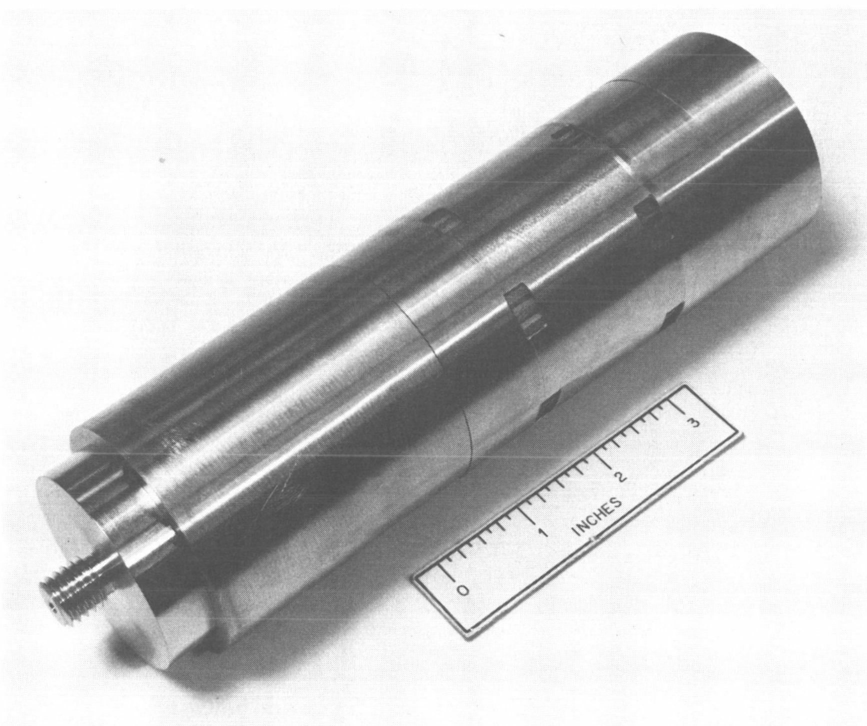
117596(C)

Figure 18. WINDOW ATTACHMENT COMPONENTS. (Three Long Rods, Not Shown, Hold the Assembly Together)



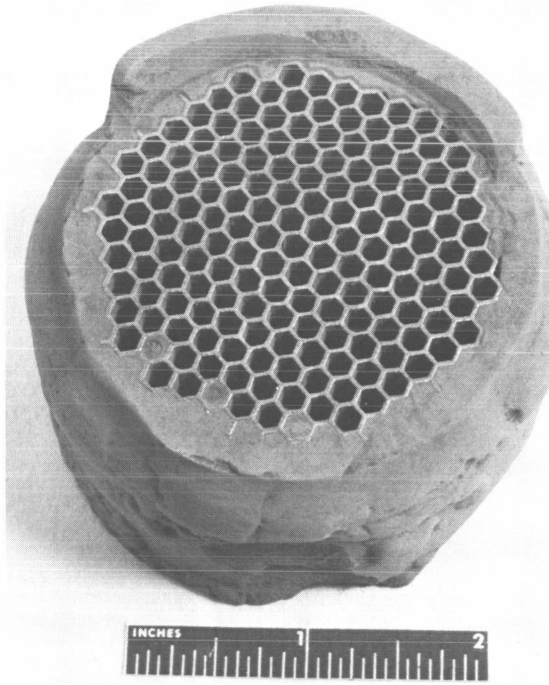

117597(C)

Figure 19. WINDOW ATTACHMENT SUBASSEMBLY.



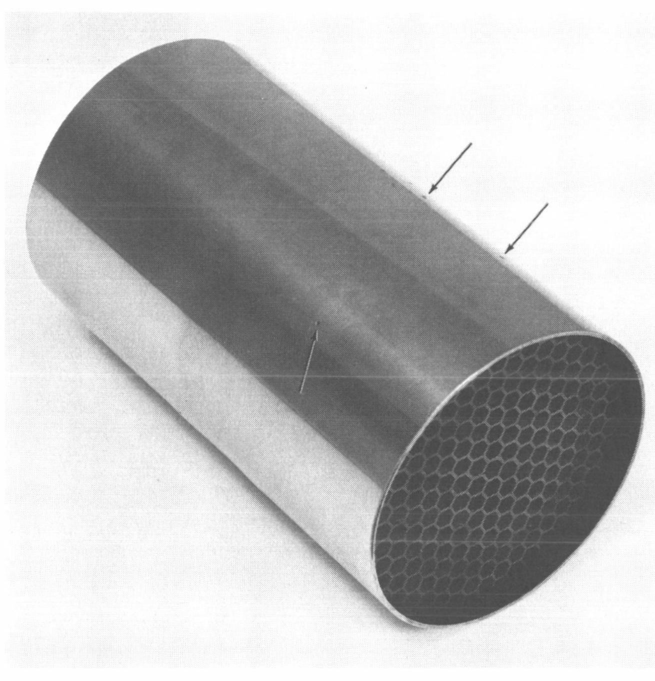

117598(C)

Figure 20. COMPLETE WINDOW ATTACHMENT ASSEMBLY.




117282(C)

Figure 21. FUEL ELEMENT PACKED WITH MOLYB-DENUM POWDER.



118668(C)

Figure 22. WINDOW ATTACHMENT AFTER DEPOSITION. (Note Holes)

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Table 1

SUMMARY OF ALL TUNGSTEN VAPOR-DEPOSITION RUNS

| Job | Mandrel Type(1) | Feed Manifold(2) | Mandrel Movement(3) | Run Time, Feed On (hrs) | $WF_6$-to-$H_2$ Flow Rate (cc/min) | $WF_6/3\ H_2$ Stoichiometric Ratio | Deposit Rate (mils/hr) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 8-Inch Bossed Tube | Moly 1 | 1 | 1/2(4) | 12/6 | $\frac{120}{4000}$ $\frac{30}{1500}$ | $\frac{1}{11}$ $\frac{1}{17}$ | ~ 3 | Good; cut to length, ground to size, mandrel dissolved; shipped. |
| One Element with a 1/4-Inch Tungsten Band in the Center | Moly 2 | 1 | 1 | 15 | $\frac{120}{4000}$ | $\frac{1}{11}$ | ~ 4 | Cracked at the tungsten band during grinding. |
| 8-Inch Bossed Tube | Moly 1 | 1 | 1 | 20 | $\frac{120}{4000}$ | $\frac{1}{11}$ | ~ 5 | Heat treated to 1130° C before grinding; cracked during heat treatment. (Probably due to the steel adapter that was screwed into the part.) |
| Two-Element Window Mount | Moly 2 | 1 | 1 | 10 | $\frac{120}{4000}$ | $\frac{1}{11}$ | ~ 2 | Sixth end final pass; still had small holes at windows. |
| Plate Window Mount Six Times to Fill Holes at Windows | | 1 | 1 | 15 | $\frac{120}{4000}$ | $\frac{1}{11}$ | - | Part was ground down to less than the finish dimensions after each deposition; holes at the windows were packed with 1-mil soft copper foil but was unable to fill all holes. |
| | | 1 | 1 | 12 | $\frac{120}{4000}$ | $\frac{1}{11}$ | - | |
| | | 1 | 1 | 12 | $\frac{120}{4000}$ | $\frac{1}{11}$ | - | |
| | | 1 | 1 | 10 | $\frac{120}{5000}$ | $\frac{1}{14}$ | ~ 4 | |
| | | 1 | 1 | 21 | $\frac{150}{5000}$ | $\frac{1}{11}$ | ~ 4.5 | |
| 8-Inch Bossed Tube | 440C-SS | 1 | 1/2(4) | 12/8 | $\frac{120}{4000}$ $\frac{40}{2000}$ | $\frac{1}{11}$ $\frac{1}{17}$ | - | Deposit split open during cooldown. |
| 8-Inch Bossed Tube | 440C-SS | 1 | 1/2(4) | 12/5 | $\frac{120}{4000}$ $\frac{40}{2000}$ | $\frac{1}{11}$ $\frac{1}{17}$ | - | Deposit shattered explosively from the mandrel shortly after removal from furnace; still slightly warm. |

(1) Mandrel Type: Moly 1 - Molybdenum pressed and sintered, solid; Moly 2 - high-density molybdenum, solid; all Type 440C stainless steel mandrels were solid.
(2) Feed Manifold: 1 - fan-type jets spraying $WF_6$ and $H_2$ directly on mandrel; 2 - 3/8-inch copper tubing with 40-mil holes—feed sprayed directly onto mandrel.
(3) Mandrel Movement: 1 - rotation plus up-down; 2 - rotation only.
(4) Desired tube wall deposited full length, then a narrow band built up at center.

[redacted]

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Table 1 (Continued)

| Job | Mandrel Type(1) | Feed Manifold(2) | Mandrel Movement(3) | Run Time, Feed On (hrs) | $WF_6$-to-$H_2$ Flow Rate (cc/min) | $WF_6/3\ H_2$ Stoichiometric Ratio | Deposit Rate (mils/hr) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 8-Inch Bossed Tube | 440C-SS | 1 | 1/2(4) | 12/5 | $\frac{120}{4000}$ $\frac{40}{2000}$ | $\frac{1}{11}$ $\frac{1}{17}$ | - | Deposit peeled at both ends at start; temperature changed (too hot) at start of the run. |
| 48-Inch Long Tube | 440C-SS | 1 | 1 | 20 | $\frac{480}{6000}$ | $\frac{1}{4}$ | ~ 3 | Good; shipped. |
| 8-Inch Bossed Tube | 440C-SS | 1 | 1 | 20 | $\frac{120}{5000}$ | $\frac{1}{14}$ | ~ 2.5 | Hairline crack at the top of the deposited tube. |
| 8-Inch Tube Mandrel Development | 440C-SS | 1 | 1 | 10 | $\frac{120}{5000}$ | $\frac{1}{14}$ | ~ 3.6 | Deposit good; cracked during grinding. |
| 8-Inch Tube Mandrel Development | 440C-SS | 2 | 1 | 8.5 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 3 | Hairline cracks in both ends of the tube. |
| 8-Inch Tube Mandrel Development | 440C-SS | 2 | 1 | 8.5 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 1.5 | Shattered; appeared to be a compressive failure. |
| Deposit One-Element Window Mount Five Times; Attempt to Fill Windows with Copper Foil also Molybdenum Powder. | Moly 2 | 2 | 2 | 16 | $\frac{30}{5000}$ | $\frac{1}{50}$ | 2 | Fifth deposit - still leaked three places at the windows under pressure. |
| | | 12 1/8-Inch Tubing; Jets Directed at Windows | 2 | 20 | $\frac{20}{4000}$ | $\frac{1}{65}$ | 3.6 at Windows | Fourth deposit - attempted to fill the window area; still had holes. |
| | | 6 1/8-Inch Tubing; Jets Directed at Windows | None | 18 | $\frac{80}{5000}$ | $\frac{1}{20}$ | 4 at Windows | Third deposit - attempted to fill the window area; still had holes. |
| | | Crimped 3/8-Inch Tube | 2 | 24 | $\frac{80}{5000}$ | $\frac{1}{20}$ | - | Second deposit - attempted to fill the window area; still had holes. |
| | | 2 | 1 | 9.5 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 3 | First deposit - holes at the window area. |

(1) Mandrel Type: Moly 1 - Molybdenum pressed and sintered, solid; Moly 2 - high-density molybdenum, solid; all Type 440C stainless steel mandrels were solid.
(2) Feed Manifold: 1 - fan-type jets spraying $WF_6$ and $H_2$ directly on mandrel; 2 - 3/8-inch copper tubing with 40-mil holes—feed sprayed directly onto mandrel.
(3) Mandrel Movement: 1 - rotation plus up-down; 2 - rotation only.
(4) Desired tube wall deposited full length, then a narrow band built up at center.

[redacted]

[redacted]



Table 1 (Continued)

| Job | Mandrel Type(1) | Feed Manifold(2) | Mandrel Movement(3) | Run Time, Feed On (hrs) | $WF_6$-to-$H_2$ Flow Rate (cc/min) | $WF_6/3\,H_2$ Stoichiometric Ratio | Deposit Rate (mils/hr) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 8-Inch Tube Mandrel Development | 440C-SS | 2 | 1 | 8.3 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 3 | This run conditioned under hydrogen at 600° C for one hour just before deposition; deposit blistered but intact. |
| 7-Inch Tube Mandrel Development (Dwg CSK-M-25800 32 √) | Black Iron (58-mil wall tube with support and cap; 1-mil copper plated.) | 2 | 1 | 8 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 2 | Would not release from the mandrel tube; dissolved mandrel and deposit broke. |
| 7-Inch Tube Mandrel Development (32 √) | Same as for Preceding Tube but with No Copper Plate | 2 | 1 | 8 | $\frac{120}{5000}$ | $\frac{1}{14}$ | 3.5 | Deposit peeled at ends but would not release; caused mandrel to go out of round. |
| One Element with a Tungsten Band on One End | 2 | 2 | 1 | 13.5 | $\frac{100}{4000}$ | $\frac{1}{12}$ | ~2.5 | Cracked at the element tungsten band during grinding. |
| Pilot 1 for First Element | 1 | 1 | 2 | 7 | $\frac{100}{4000}$ | $\frac{1}{12}$ | ~3 | Good. |
| Pilot 2 for First Element | 1 | 1 | 2 | 11 | $\frac{100}{4000}$ | $\frac{1}{12}$ | ~3 | Good. |

(1) Mandrel Type: Moly 1 - Molybdenum pressed and sintered, solid; Moly 2 - high-density molybdenum, solid; all Type 440C stainless steel mandrels were solid.
(2) Feed Manifold: 1 - fan-type jets spraying $WF_6$ and $H_2$ directly on mandrel; 2 - 3/8-inch copper tubing with 40-mil holes—feed sprayed directly onto mandrel.
(3) Mandrel Movement: 1 - rotation plus up-down; 2 - rotation only.
(4) Desired tube wall deposited full length, then a narrow band built up at center.

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carbon steel, and one on carbon steel. The feed manifold on the initial stainless steel mandrel utilized fan-type jet spray nozzles, and the remainder utilized a 40-mil hole manifold. The mandrel movement in all tests was both circumferential and longitudinal. The flowrate in all tests was 120 cc/min for the tungsten hexafluoride and 4000 cc/min for the hydrogen resulting in a fluoride-to-hydrogen ratio of 11 times stoichiometric hydrogen. The deposition rate varied from 1.5 to 3.6 mils per hour. On one run using the stainless steel mandrel, the part was removed from the mandrel intact; however, it cracked during the grinding operation. On the other three stainless steel mandrel runs, the deposit on one shattered, blistered on another, and contained hairline cracks on the third. On both carbon steel mandrel runs the deposit would not release from the mandrel.

## Forty-Eight-Inch Tube

One 48-inch tube was deposited on a Type 440C stainless steel mandrel. Fan-jet spray nozzles were used with a mandrel movement in both the circumferential and longitudinal directions. A flow rate of 480 cc/min for the tungsten hexafluoride and 6000 cc/min for the hydrogen resulted in a fluoride-to-hydrogen stoichiometric ratio of 1 to 4. The deposition rate was approximately 3 mils per hour. This mandrel and support tube are shown in Figure 23. The tube was considered specification quality and shipped.

## Eight-Inch Bossed Tubes

Six deposition runs were made on 8-inch bossed tubes. Two of the runs utilized pressed and sintered molybdenum mandrels and the remainder utilized Type 440C stainless steel mandrels. All runs were deposited with fan-type jet spray nozzles with mandrel movement in both the circumferential and longitudinal directions. The boss on four of the units was deposited with the mandrel fixed in the vertical position and rotated. A flow rate of 120 cc/min for the tungsten hexafluoride and 4000 cc/min for the hydrogen (1 to 11 stoichiometric ratio) was used for the initial deposit on five of the units; the hydrogen flow rate was increased to 5000 cc/min (1 to 14 stoichiometric ratio) on the sixth unit. A flow rate for redepositing the boss was 30 cc/min for the tungsten hexafluoride and 1500 cc/min for the hydrogen on one unit, and 40 cc/min for the tungsten hexafluoride and 2000 cc/min for the hydrogen on the other three units. A stoichiometric ratio of 1 to 17 was obtained on all units. The deposition rate ranged from 3 to 5 mils per hour. Figure 16 shows a finished 8-inch tube with a boss. Of the six deposited units, one was considered to be of specification quality and was shipped. Of the remainder, the deposit cracked on one during heat treatment, split during cooldown on another, shattered explosively on the third, peeled at the ends on the fourth, and contained hairline cracks on the fifth.

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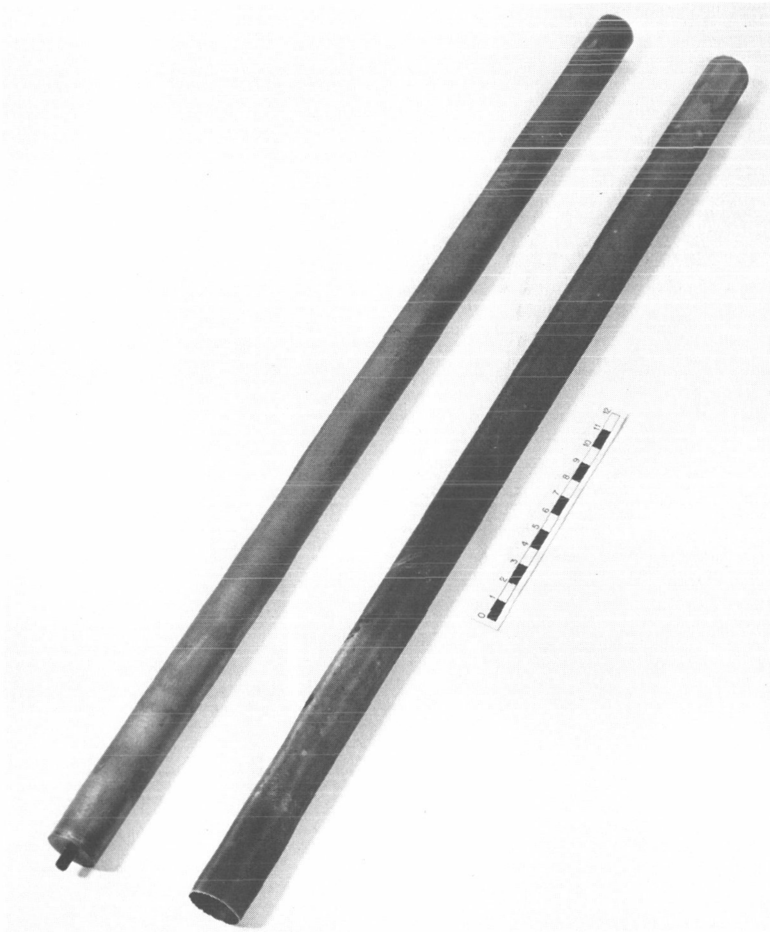

118284(C)

Figure 23. FORTY-EIGHT-INCH TUBE.

Single-Element Assembly with Center Band

One deposition run was made with a tungsten band at the center of the fuel element. The mandrel was made from commercial-grade, high-density molybdenum. A fan-jet spray nozzle manifold was employed with mandrel movement in both the circumferential and longitudinal directions. A flow rate of 120 cc/min for the tungsten hexafluoride and 4000 cc/min for the hydrogen resulted in a stoichiometric ratio of 1 to 11. The deposition rate was approximately 4 mils per hour. A view of this assembly is presented in Figure 9. The deposit as well as the tungsten band cracked at the tungsten band during the grinding operation.

Single-Element Assembly with End Band

One deposition run was made with the tungsten band at the end of the fuel element, as shown in Figure 12. The same type of mandrel and mandrel movement was used as

[redacted]



with the center-band unit. The feed was through a 40-mil hole manifold at a rate of 100 cc/min for the tungsten hexafluoride and 4000 cc/min for the hydrogen, or a stoichiometric ratio of 1 to 12. The deposition rate was approximately 2.5 mils per hour. The deposit cracked at the tungsten band that was used to support the tube interface during the grinding operation. Prior to depositing this unit, two pilot runs were made using essentially the same parameters and with good results.

Single-Element Assembly with Windows

One deposition run was attempted with a commercial-grade molybdenum mandrel. The vapor-deposition gas was fed through a 40-mil hole manifold and with mandrel movement in both the circumferential and longitudinal directions. A flow rate of 120 cc/min for the tungsten hexafluoride and 5000 cc/min for the hydrogen (1 to 14 stoichiometric ratio) was maintained, and a deposition rate of 3 mils per hour resulted. At the conclusion of the run, the deposit contained holes in the window area. This unit was redeposited four times but the unit still leaked under pressure at three places in the window area.

Two-Element Assembly with Windows

The same results were obtained as with the single-element window unit. Holes in the window area were still present after a total of six deposition runs. Approximately the same parameters were used as on the single-element assembly with the centrally located band. Figure 18 shows the components of a two-element assembly with the window design. A typical hole which persisted after numerous deposition attempts is shown in Figure 22.

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# RECOMMENDATIONS AND SUMMARY

## RECOMMENDATIONS

The following areas should be investigated:

1. Metering hexafluoride can be improved. A range of hexafluoride-to-hydrogen ratios should be further investigated to better determine the optimum ratio for efficient quality depositing. The possibility of using tungsten hexachloride should also be studied.

2. Procedures should be developed for cleaning and other surface-preparation operations such that if deposition is discontinued and then restarted there will be a minimum disturbance of the microstructure at the interface between the new and old deposit.

3. A method should be developed that will reduce the bond strength between the vapor-deposited tungsten and the mandrel to a point where thinner parts can be deposited and removed from the mandrel successfully. (Consideration has been given to colloidal graphite as the parting agent, but a single run in which it was tried aborted.)

4. Search for more versatile and less-expensive mandrel materials, and better utilization of the present mandrel materials.

5. Investigate other materials that might be applicable for support-tube fabrication and use in a reactor.

6. A filler material should be developed for the open cells of the fuel elements to further perpetuate the window-attachment technique. Considerations should include a molybdenum powder with a polystyrene binder and pressureless packing of molybdenum powder around the fuel element followed by sintering.

## SUMMARY OF RESULTS

Although most of the vapor-deposition parameters have not been optimized, the present starting parameters are recommended, namely:

1. Stoichiometric ratio of tungsten hexafluoride to hydrogen should be 1 to 15 ($\sim$ 1 to 45 by volume).

2. The deposition rate should be 3 to 4 mils per hour and the temperature $\sim 600^\circ$ C.

3. The mandrel should be of high-density pressed and sintered molybdenum.

If a practical technique for preparing the fuel-element surface can be devised, it appears that the window-deposition method will be a satisfactory attachment technique.

Vapor-deposited tungsten can be: (1) ground to precision tolerances, but the fragility of the material must be recognized; (2) made into intricate parts; (3) heat treated to have mechanical properties similar to wrought material.